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formance. The use of "Fortifiers" in conjunction with rubber modifiers provides an attractive combination of stiffness, strength and fracture toughness, and offers particular advantages in low-to-medium cure temperature adhesive formulations. "Fortifiers" also provide benefits in adhesive bond performance when applied as primers to steel surfaces, presumably by stiffening and strengthening the interfacial region. The molecular basis of the property modification is discussed.

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The Use of "Epoxy Fortifiers" in Adhesive Applications

Interim Technical Report

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## The Use of "Epoxy Fortifiers" in Adhesive Applications

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### ABSTRACT

Additives for epoxy resins called "epoxy fortifiers" (US Patents 4480082, 4,739,028) increase the stiffness and strength of crosslinked epoxy resins, and modify their fracture characteristics such that they fail in a ductile fashion under tensile loading. The improvements in adhesive bond performance which result from improved bulk adhesive properties are reviewed. Other benefits of "fortifier" addition can include acceleration of the cure, a reduction in coefficient of thermal expansion, and a reduction in the rate of water uptake. Drawbacks of "fortifier" addition can include a reduction in pot life, and a reduction in glass transition temperature. It should also be cautioned that although ductile failure occurs in a tensile test, and fracture toughness ( $K_{IC}$ ) is increased, the toughness after "fortifier" addition is still significantly less than for rubber modified systems. Adequate interfacial adhesion also is a prerequisite for "fortifier" addition to translate into improved adhesive bond performance. The use of "fortifiers" in conjunction with rubber modifiers provides an attractive combination of stiffness, strength and fracture toughness, and offers particular advantages in low-to-medium cure temperature adhesive formulations. "Fortifiers" also provide benefits in adhesive bond performance when applied as primers to steel surfaces, presumably by stiffening and strengthening the interfacial region. The molecular basis of the property modification is discussed.

### INTRODUCTION

This Interim Technical Report was prepared at the request of the Army Research Office, as a part of project number 25760-MS. It is intended to review the use of existing "epoxy fortifier" formulations in adhesive applications, including the work at the University of Connecticut during the first six months of the ARO project. The report also summarizes briefly the state of understanding of the molecular basis for the property modification.

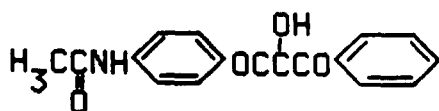
The term "epoxy fortifier" is a non-scientific name describing a family of additives for epoxy resins which increase the stiffness and strength of the cured resins, and modify their mode of failure (1-6). These materials were developed mostly at the National Research Council of Canada and are subject to patent protection. The NRCC project team is now largely dispersed, and the author of this report is continuing research on academically interesting aspects of the phenomenon at the University of Connecticut. Commercialization has progressed slowly for several years, first by Uniroyal Ltd of Guelph, Ontario, and now by Polysar Corporation of Sarnia, Ontario (point of contact - Mr. Lasse Vainio, Corporate Research and Development Division, Polysar Corp, North Front Street, Sarnia, Ontario N7T 7M2, Tel 519

337 8251). The original intended application of these materials was in organic matrices for composite materials, and their utility in this application has been demonstrated (4). However, in addition to increasing stiffness and strength, epoxy fortifiers also show beneficial effects in terms of reduced cure temperature, water sorption, and coefficient of expansion, making them of considerable interest in adhesive applications (4-6). In this regard, Industrial Formulators Ltd., of Vancouver, British Columbia, in collaboration with Dr. G. Luoma of the Defence Research Establishment Pacific (DREP), Victoria, British Columbia, have developed adhesive formulations, based upon fortifier technology, which show considerable promise in applications involving the repair of military equipment (7). The ARO project "Modified Epoxy Adhesives and Primers" (Andrew Garton, P.I.), is intended to explore the molecular basis and utility of "fortifiers", particularly in adhesive and primer applications, and to extend the range of polymers to which this means of property modification can be usefully applied.

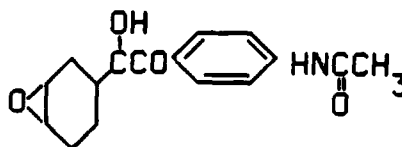
#### CHEMICAL COMPOSITION OF FORTIFIERS

The commercial formulations developed by Polysar Corporation (Fortifiers EF-10, EF-15, EF-20) and by Industrial Formulators Ltd. are proprietary. The patents (1,2) describe reaction products of substituted aromatic amides, polyhydroxy compounds, or amines with either monoepoxides (e.g. epoxyphenoxypropane, EPP) or unsymmetrical diepoxides (e.g. vinyl cyclohexene dioxide, VCD). In general, these are low melting point solids which are mixed with the resin and curing agent immediately before curing. The synthetic procedures and full details of the mixing and curing of the epoxy resins are available elsewhere (1-6). Their chemical compositions are complex.

Publications in the open literature have concentrated mostly on the additive compositions, EPPHAA and VCDHAA (3-6). The additive EPPHAA is the reaction product of 4-hydroxyacetanilide (HAA) and EPP, at a 1:1.05 mole ratio, heated to 160°C for 60 minutes in the presence of 0.1% diethylamine hydrochloride catalyst. The chemical composition has been determined to correspond to structure I (3). VCDHAA is the reaction product of VCD and HAA, at a mole ratio of 1.5:1, and is thought to consist largely of structure II. The most noticeable difference between the two structures is that VCDHAA has residual epoxy functionality, and so can become chemically bonded to the crosslinking polymer, while the additive EPPHAA can be extracted from the pulverized polymer with a solvent, and so is not chemically bonded (3).



I



II

## BULK PROPERTIES OF "FORTIFIED" EPOXIES

The fortifier is mixed with the epoxy resin and curing agent just prior to use. Considerable effort has been expended in the commercialization to produce materials which are easily processible with conventional epoxy systems. For example, the melting point of the additives usually does not exceed  $100^{\circ}\text{C}$ . Figure 1 shows the tensile stress-strain curves for the unmodified epoxy (Epon 828/MDA), and specimens containing 20 and 30 phr EPPHAA. There is an increase in tensile strength from about 80 MPa to about 105 MPa and 120 MPa, together with an increase in tensile modulus from 2.5 GPa to about 4.0 GPa. The overall strain to break is decreased slightly by the additive, although the yielding evident in the tensile curve implies that local strains may be very high.

An examination of the fracture surface of specimens (b) and (c) in Figure 1, confirms that extensive local plastic deformation occurred during the yield process, producing fracture surfaces characterized by shallow cavities of about 100 micron diameter, surrounded by ridges of highly deformed material (3).

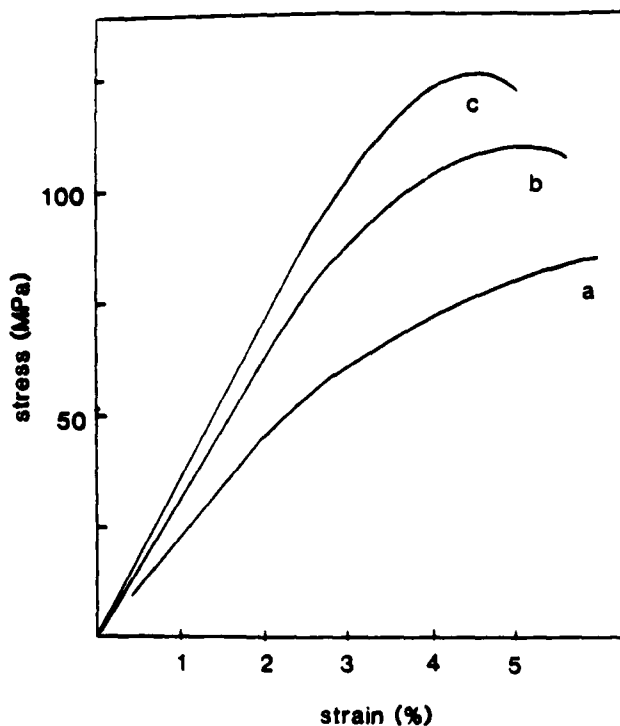


Figure 1 Engineering stress-strain curves: (a)Epon 828/MDA  
(b)+20phr EPPHAA (c)+30phr EPPHAA

We have constructed a shear strength test facility (ASTM D732) and observe a qualitatively similar increase in shear modulus and strength. For example, 20 phr VCDHAA increased the shear strength from 9,250 psi to 10,350 psi.

We are presently constructing a compression test fixture, to complete the bulk property characterization. Other mechanical property measurements reported elsewhere (4) include fracture toughness (miniature compact tension specimens). For a specimen containing 30phr EPPHAA, the value of  $K_{IC}$  was about 60% higher than the control at low testing speeds, but approximately equal to the control at higher testing rates. It should be noted, however, that the values for  $K_{IC}$  ( $< 2 \text{ MN/m}^{3/2}$ ), obtained with EPPHAA in an epoxy system without rubber modification, are significantly less than those obtained for rubber toughened systems, and so it may be misleading to call these materials "tough" in the conventional sense.

Figure 2 shows that the additive EPPHAA facilitates curing of Epon 828/MDA at low temperatures, which has obvious relevance to adhesive applications. Thus, a tensile strength of almost 120 MPa, and a tensile modulus of  $> 3.5 \text{ GPa}$  are achievable with a  $60^\circ\text{C}$  cure temperature. Furthermore, the improved stiffness and strength are retained even on exposure to environmental aging. For a specimen containing 30 phr of a fortifier consisting of the reaction product of VCD and aniline (5), a tensile strength of about 107 MPa was retained after 8 days at  $75^\circ\text{C}$  and 95% relative humidity, while the strength of the control specimen had degraded to about 70 MPa. On drying, the tensile properties returned to close to their original values (4-6).

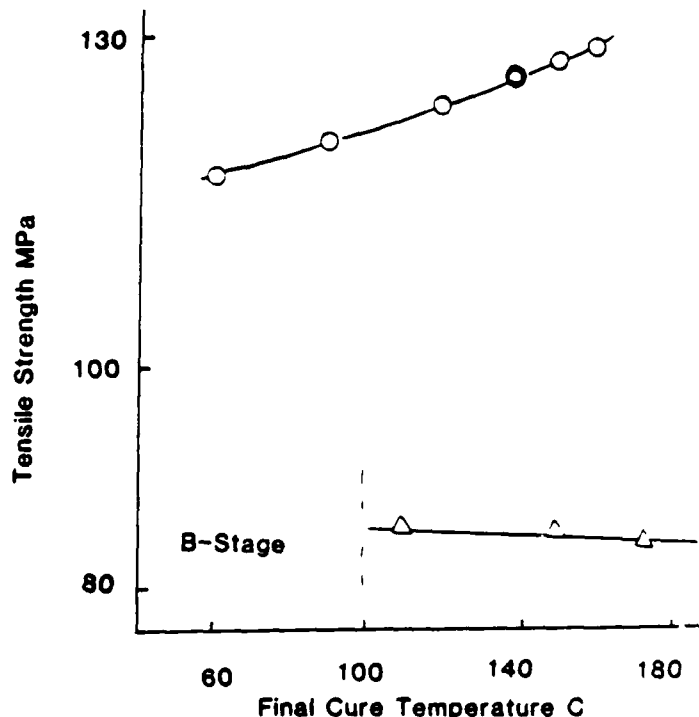


Figure 2 Tensile strength as a function of cure temperature for Epon 828/MDA:  $\Delta\Delta$  control,  $\circ\circ$  +30 phr EPPHAA

The good environmental stability is reflected in the water uptake characteristics of the cured polymer. Figure 3 demonstrates that 20 phr of additive VCDHAA reduces the water uptake by

about 20%. Note that the test was carried out at room temperature. At higher temperatures the benefits are less apparent because of the reduction in  $T_g$  associated with the addition of some fortifiers (see below).

The final bulk polymer property highlighted here because of its relevance to adhesive applications is the coefficient of thermal expansion (CTE). The thermal expansion characteristics of a glassy polymer depend in a complex fashion on the thermal history of the specimen, but Figure 4 shows that for specimens cooled slowly from the rubbery state ( $1^\circ\text{C}/\text{min}$ ), the addition of fortifiers reduces the CTE of the glassy polymer. In the case illustrated here, this effect is counterbalanced by a reduction in  $T_g$ , but other higher  $T_g$  formulations show similar behavior. For specimens with different thermal histories, the reduction in CTE can be appreciably greater and we are presently exploring this phenomenon in greater depth, both by conventional thermomechanical analysis and (for thin films) using a modification of the Polymer Laboratories Dynamic Mechanical Analyzer.

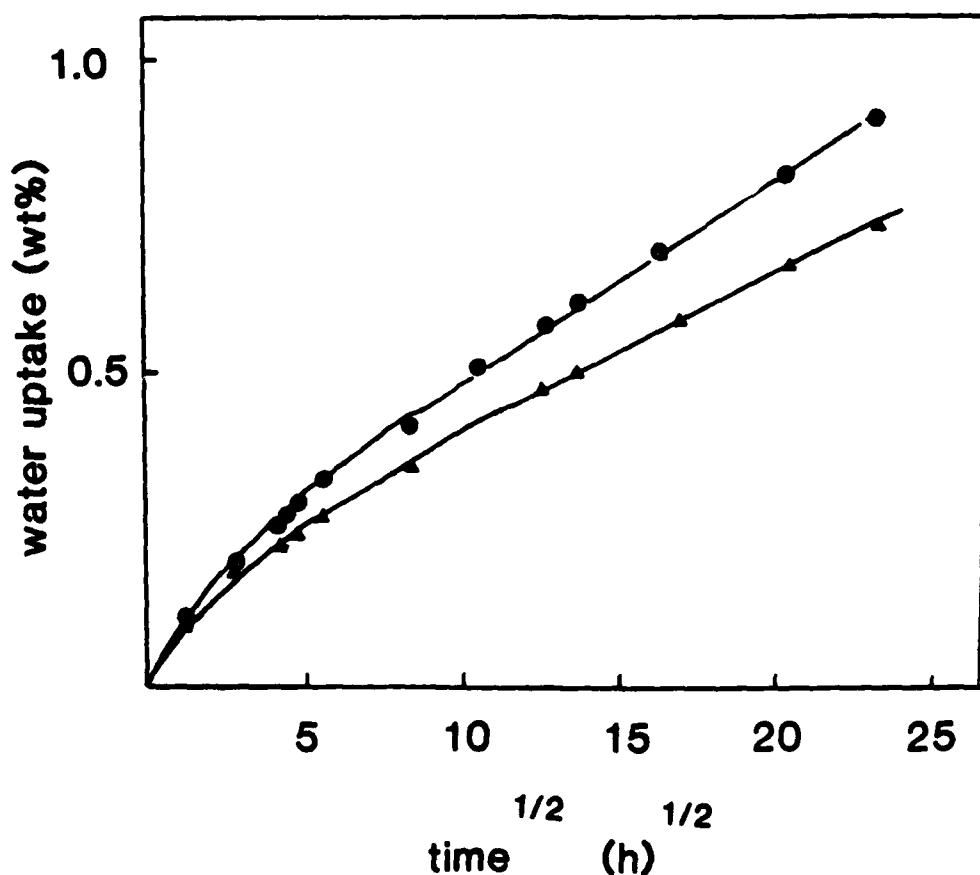
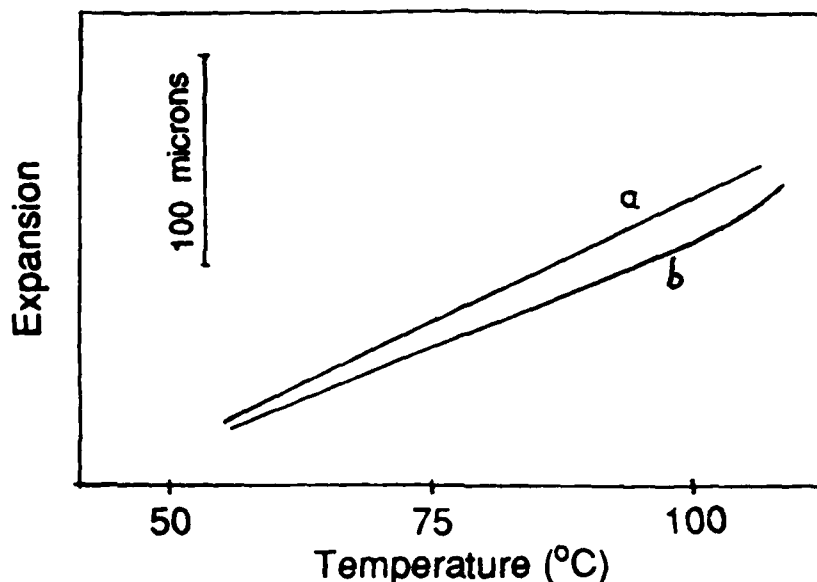


Figure 3 Gravimetric determination of water uptake in 95% humidity air at  $25^\circ\text{C}$ . ●● control, ▲▲ +20phr VCDHAA



Figure 4 Thermal expansion at 5°C/min heating rate. (a) control  
(b) +20phr VCDHAA



#### PROPERTIES OF ADHESIVE JOINTS

A napkin ring torsional joint geometry was selected for the structural joint study, because the stresses associated with this geometry are relatively simple (largely shear) and uniform (8). The adhesive-substrate contact area is also greatly reduced in comparison with the lap shear joint geometry, with the result that water resistance can be tested over much shorter periods. The steel substrates were prepared for bonding by using trichloroethylene degreasing, followed by ammonium citrate (ammoniated citric acid, pH = 4) treatment at 75°C for 10 minutes. A distilled water bath followed by a methanol bath completed the treatment. The surfaces were air dried prior to bonding. Selected steel substrates were also dipped into acetone solutions of VCDHAA in acetone/methanol (concentration 0-25 wt%) to apply a thin coating of the additive as a primer.

The majority of the data refer to an Epon 828/MDA system (30phr MDA) without rubber modification, because of the large amount of background information available on this system. However, the effect of rubber modification was explored for some specimens by prereacting 15 phr of CTBN (B.F. Goodrich, 1300X8) with the epoxy resin (pre-reacted as a concentrate in the resin for 4h at 80°C, using Triphenyl phosphine catalysis). For both resin systems, exactly 44 mg of the mixture was applied to the annular ring of the joint, using a small disposable syringe with a 21 gauge needle. The two sides of the joint were brought together and placed in a steel sleeve to ensure proper alignment. The joints were cured in a vertical position, usually for one hour at 120°C, followed by two hours at 150°C, although for one set of specimens the effect of a reduced cure temperature (3 hours at 80°C) was examined. To test the water resistance, the joints were

immersed in 57°C distilled water for known periods of time, with constant bubbling of nitrogen, allowed to cool to 25°C and then tested on an Instron tensile tester equipped with a torsional test fixture.

Table I summarizes some of the steel joint performance data. Briefly, the shear strength of the joints increased with increasing shear strength of the resin, although not in direct proportion. The limits of scatter of the data are shown in Figure 5, and each data point in Table I represents the average of at least 3 but in some cases up to 12 specimens. We realize that such sampling sizes are insufficient for an accurate specification of material performance, but our intention here is to obtain trends and test mechanistic hypotheses, not to perform an engineering evaluation. The shear forces involved in a joint of this type can be close to the shear strength of the bulk adhesive (9), and so improvements of an order of magnitude in joint strength cannot be expected. The strength improvements shown for the 150°C cured specimens follow the expected increase in bulk shear strength at low additive concentrations, but clearly a limit is reached which we feel is defined by the strength of the interfacial region (30 phr I adhesive joint < 20 phr adhesive joint, while 30 phr I bulk strength > 20 phr bulk strength). The benefits of fortifier addition become more apparent for the low temperature cured specimens, because the controls against which the fortified specimens must be compared are significantly inferior to the high temperature cured controls (Epon 828/MDA does not cure satisfactorily at < 100°C).

Rubber modification of the epoxy reduces the shear strength of the bulk adhesive (e.g. 9,250 psi for the control and 7350 psi for the rubber modified), as expected, and so reduces the strength of the adhesive joint control, but the benefits of fortifier addition are again apparent. This is particularly encouraging for other joint geometries and test conditions (e.g. lap shear, wedge, or peel) where the benefits of rubber addition would be more apparent, while the deleterious effects of a decreased shear modulus and strength would be reduced by fortifier addition. It is also noteworthy that the bulk shear strength of the rubber modified epoxy is increased by the addition of 20phr VCDHAA (shear strength 9,350 psi, modulus increase >20%), which implies that there may be other application areas (e.g. structural supports) where a combination of fortifier and rubber modifier may be useful.

Table 1 Adhesive Joint Performance (normalized failure loads)

150°C Cure		80°C cure		Rubber Mod		VCDHAA primer	
control	100	control *	43	control	74	control	100
+20phr I	120	+30phr I	106	+20phr	89	7% sol #	123
+30phr I	117			VCDHAA		11%	116
+20phr	128					18%	67
VCDHAA						25%	36

\* Epon 828/DETA

# conc. of primer solution

An increase in adhesive joint strength with increased bulk adhesive strength presupposes that interfacial adhesion is adequate to allow transfer of the stresses to the bulk adhesive. Microscopic examination of the failed joints shows that failure occurs at or near the interface, and so we explored the localized stiffening and strengthening of the interfacial region by the use of VCDHAA as a primer. Interdiffusion with the adhesive should produce a layer several microns thick with a modulus and strength higher than that of the bulk adhesive. Table I shows that this approach is almost as effective as modification of the bulk adhesive, provided the thickness of the primer layer is optimized. If it is too thin, the primer layer will be overly diluted by the adhesive. If it is too thick, insufficient interdiffusion will occur and the strength of the interfacial region will drop.

The importance of good interfacial adhesion is emphasized in Figure 5, which illustrates the effect of environmental aging. After 100h immersion in hot water, the interfacial properties of the joint have deteriorated to the point that the benefits of fortifier addition are negated. We are presently examining the interfacial stability of adhesive joints made with VCDHAA primer.

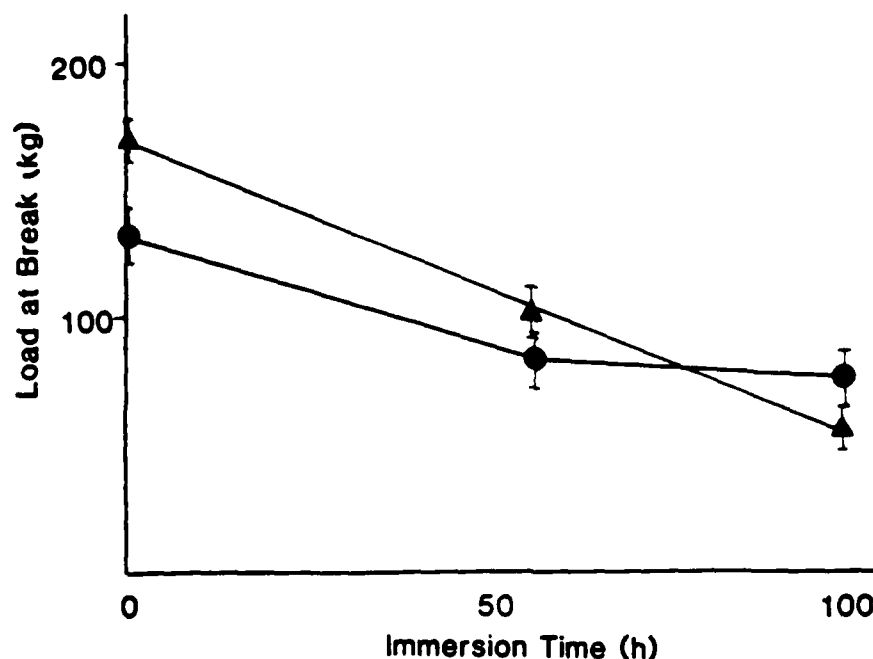


Figure 5 The Effect of Immersion in Water at 57°C on Joint Strength ●● control ▲▲ +20phr VCDHAA

The data from reference 7 are also summarized here for comparison with our napkin ring joint data. Luoma (7) describes proprietary formulations based on fortifier technology. Significant improvements in lap shear strengths (single and double, aluminum and titanium) and cleavage strengths were observed for specimens prepared by either sanding or etching. For example, the cleavage strength of an epoxy adhesive with etched aluminum adherends was doubled by modification of the adhesive formulation

both by fortifiers and rubber additives. Marked improvements are reported over commercial adhesive systems such as FM300 and EA9321. Benefits were particularly apparent when compared to conventional low temperature cure systems. Another interesting aspect of the results in reference 7 is the relative insensitivity of the joint strength to the mode of surface preparation for certain of the adhesive formulations. Some data are presented concerning weathering of adhesive joints, confirming that joints made with etched aluminum have greater environmental stability than joints made with sanded aluminum. However, no data are presented concerning fatigue and durability performance.

#### MOLECULAR BASIS OF PHENOMENON

Some progress has been made concerning the molecular basis of fortifier action, particularly with respect to the additive EPPHAA (3), and to a lesser extent VCDHAA. The individual aspects of property modification (i.e. stiffness, failure mode, cure acceleration) are best considered separately.

The increase in modulus (Figure 1) can be best explained in terms of the concept of antiplasticization (3-6,9). When a low molecular weight material is added to a polymer, the resultant free volume of the system ( $f$ ) can be described by the relationship (10):

$$f = V_1 f_1 + V_2 f_2 + KV_1 V_2$$

where  $V_1$  is the volume fraction of the polymer and  $f_1$  is the fractional free volume of the polymer, while  $V_2$  and  $f_2$  refer to the additive. The most common case (plasticization) is that the small molecule additive has a high  $f_2$ , while  $K$  is negative but small, and so a free volume increase occurs. If, however, the additive is a stiff polar molecule, a combination of a low  $f_2$  and a large negative  $K$  can cause the free volume to decrease. Such a phenomenon has been reported for several glassy thermoplastics (9,11-13), and usually results in an increase in modulus but a catastrophic decrease in strain to break (i.e. embrittlement). The antiplasticization of crosslinked polymer has been less widely studied. Hata et al (14) describe the addition of polychlorinated biphenyls (PCBs) and oligomeric species to an amine cured epoxy resin, as have several Russian authors (15,16). The relatively small increase in modulus, combined with the environmental unpopularity of PCBs and the marked depression in  $T_g$ , led to a decrease in interest in this area.

Evidence to support this mechanism of stiffening includes the suppression of low temperature relaxations of the network (3), and the apparently negative volume of mixing of the polymer and the additive (Figure 6), both of which are characteristic of antiplasticization. The additive EPPHAA does not become chemically bound to the crosslinked epoxy matrix (3), and does not affect the final extent of epoxy consumption, which makes an explanation based upon a modified network structure seem less likely. More recently, in collaboration with Dr.W.Stevenson of Wichita State University, we have confirmed this free volume reduction hypothesis by positron

annihilation studies. On exposure of specimens of epoxy resins to a positron source, the fraction of annihilations which took place as ortho-positronium species was reduced significantly when a fortifier was present (30.1% compared to 34.7%) which implies that less free volume was available for stabilization of the longer-lived orthopositronium, and so more annihilations took place either as free positrons or parapositronium species. A comparison with the results of Y.C.Jean et al (17) indicates that the size of the free volume "holes" in this aromatic amine cured epoxy system is  $< 0.03 \text{ nm}^3$  (i.e. smaller than in the more commonly studied glassy thermoplastics and aliphatic amine cured epoxies), which is at the lower limit of where current positron annihilation techniques and theories are useful in a quantitative sense. Some further development of the technique is therefore necessary if positron annihilation is to be more useful in quantitative analysis of free volume in our specimens.

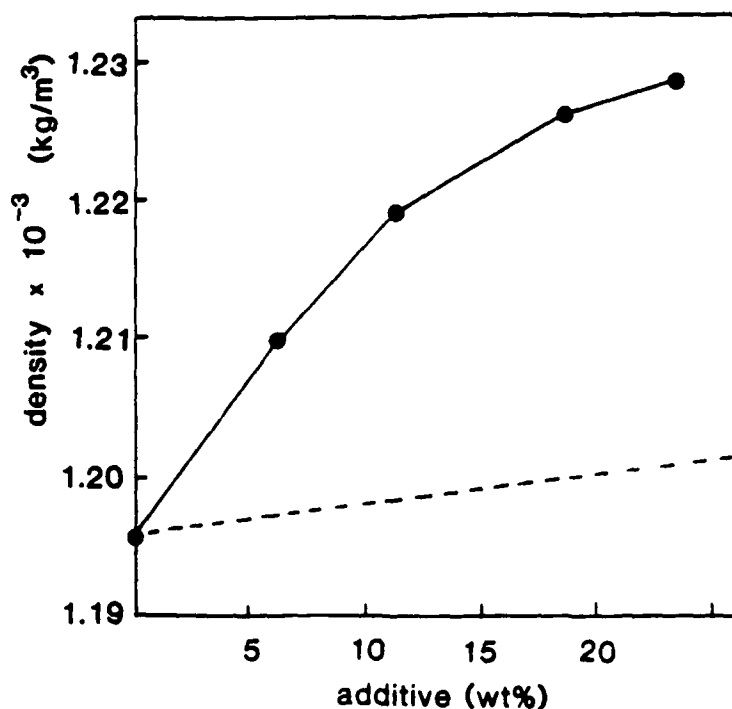


Figure 6 Density of the Cured Polymer. Dashed line denotes the density calculated assuming additivity of the densities of the polymer and of EPPHAA

The occurrence of a marked yield point and strain softening in the fortified epoxy specimens (Figure 1) is more surprising. As a general rule, an increased modulus tends to be associated with increased brittleness. We can explain the yielding on a semi-quantitative basis by the following model, although we realise that this is a far from complete picture of the many factors which affect the failure characteristics of glassy polymers.

Figure 7 shows that there is a considerable increase in volume ( $\Delta V_{\text{strain}}$ ) as a tensile specimen is subjected to tensile

strain (the volume was measured with perpendicularly aligned strain gauges). The volume increase with the fortifier present is at least 20% greater than the control. As a first approximation, we can equate this volume increase to that produced by an increase in temperature from  $T$  to  $T'$  where  $T'$  is now a fictive temperature. If the proportion of the volume increase in each case that can be considered as free volume increase is similar, and if a system is considered solely to be defined by its free volume, then increasing strain can be equated with an increase in fictive temperature. At a certain strain, sufficient free volume will be introduced for the specimen to pass through the glass to rubber transition ( $T_g$ ) and so bulk yielding will occur.

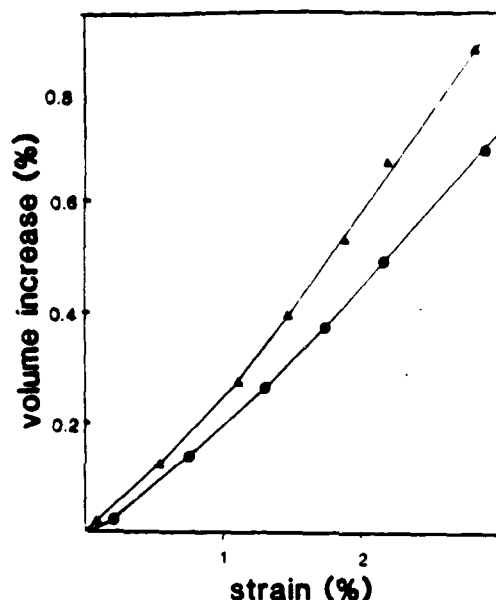


Figure 7 Volume change which occurs during a tensile test

● ● control ▲ ▲ +30phr EPPHAA

This model may be quantified further if the volume change data of Figure 7 are compared with thermal expansion data (e.g. as in Figure 4). For the specimen containing 30phr EPPHAA, the relationship between strain and fictive temperature is shown in Figure 8. At strains greater than about 4%, the fictive temperature begins to approach the glass transition temperature of the polymer (about 105°C in this case) and so yielding can be expected. The extent of yield however will be constrained by the crosslinked nature of the polymer, and so the formation of a macro-neck, as occurs in thermoplastics, cannot be expected. In the case of the control specimen, the strain induced volume increase is less than for the fortified specimen, and the thermal volume increase on rising to  $T_g$  is greater, and so a much greater strain is necessary to induce the glass to rubber transition. We have demonstrated elsewhere that other fortified systems with higher  $T_g$ 's follow a similar semi-quantitative relationship (5,6).

While this model is attractive in its simplicity, it does not consider the complexity of polymer fracture mechanisms (18,19). Strain softening, if it is confined to a localized region, will

lead to premature failure by a crazing mechanism. Such behavior will be particularly important in a tensile test because of the dilatational component of the tensile stress. The presence of sharp defects will lead to localized stress concentrations, which will tend to further localize the strain softening, and so the failure mode will be dependent on the distribution of defects in the specimen, as we have considered previously (5). The tensile curves and fracture surfaces obtained from fortified epoxies (3-6) imply that at least in our well prepared tensile dogbones, the strain softening is sufficiently delocalized that considerable yielding can occur. An alternative way of looking at the phenomenon is to ask why is the onset of crazing inhibited. It is to answer these and other questions that we are presently involved a more detailed examination of the bulk polymer response to a variety of stresses, including shear and compression.

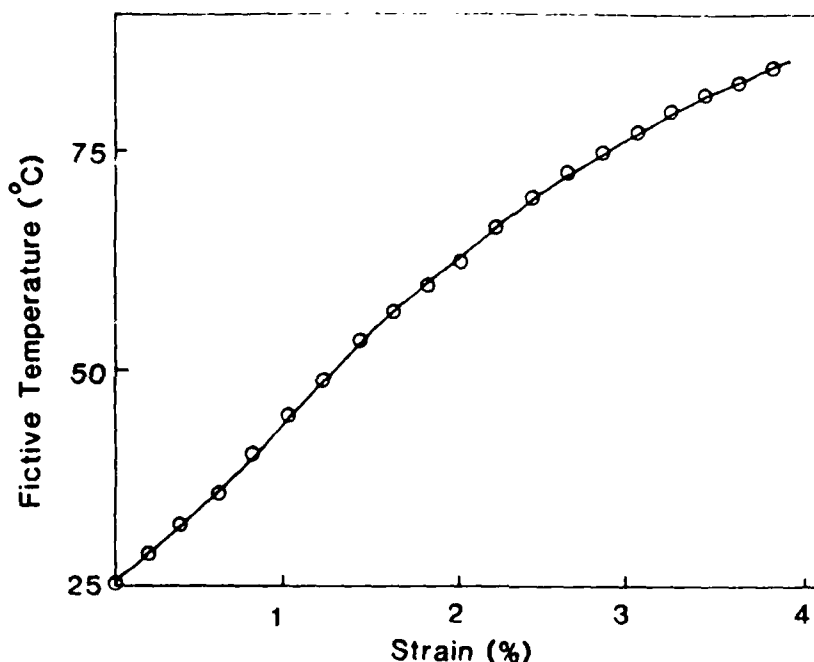


Figure 8 Fictive temperature vs. tensile strain for specimen containing 30 phr EPPHAA

Several other aspects of bulk polymer properties are amenable to rationalization by a free volume model. A reduced rate of water sorption (Figure 3) would be directly related to a decrease in the free volume required for penetrant migration. It should be cautioned, however, that many fortifier formulations contain polar or hydrophilic groups and so equilibrium water contents (if such a parameter has any real meaning) may increase. A decrease in coefficient of thermal expansion (Figure 4) will be related to free volume considerations, but not necessarily in a straightforward way. We have observed a strong dependence of CTE on the prior thermal history of the specimen, and are presently examining this behavior in more detail, both as a probe of free volume and because of the obvious relevance of CTE to adhesive bond performance.

We attribute the accelerative effect on cure rates of fortifier addition to a combination of physical and chemical factors. Hydroxyl and other polar functional groups are well known to increase the rate of epoxy-amine reactions (20). Also, when the mixture is in the liquid and rubbery states, the additive will function as a diluent and so decrease the local viscosity. The relative importance of the two processes will vary with the state of cure.

### FUTURE DIRECTIONS

Obviously we cannot comment upon the future plans of those involved in the commercialization of these additives. This section describes in general terms research opportunities identified in the first phase of the ARO project # 25760-MS which are either presently being studied or will be studied in the next twelve months.

Now that at least some testing protocols have been adequately defined, we consider that the next crucial step is the preparation and isolation of reasonable quantities of a purified reactive fortifier of the type illustrated as structure II (page 2). Our goal is then to determine by a variety of chemical and spectroscopic means the pathways for incorporation of this additive into the epoxy network, and the structure of the crosslinked polymer. In particular, we wish to determine whether the additive reacts concurrently with network formation, and so produces "loose ends" in the network, or whether the cycloaliphatic epoxy reacts with hydroxy functionality on the preformed epoxy-amine network. Liquid chromatography can provide us with precise quantitative information in the early stages of the cure, and even after gelation provided solvent extraction is used. We also hope to be able to distinguish alicyclic epoxy functionality from aliphatic epoxy functionality by infrared spectroscopy, and so obtain access to the later stages of the cure cycle.

In terms of cured epoxy structure and properties, we feel one of the most informative characterization techniques will be dynamic mechanical analysis (DMA). We have already confirmed that a crude VCDHAA formulation suppresses the low temperature transitions of the epoxy network. With networks prepared under more controlled conditions, we plan to place this measurement on a more quantitative basis. We have recently purchased the Polymer Laboratories DMA, and this instrument gives us the opportunity to pre-stress our specimens to a significant fraction of the yield stress before subjecting them to a small sinusoidal strain. In such a way we can test our hypothesis that tensile strain can increase free volume in our specimens to such a degree that the fictive temperature approaches the glass transition temperature.

A better characterized starting material with a known thermal history will also allow us to explore with more confidence the effect of these additives on the CTE of the cured matrix. A recently purchased programmable oven will allow us to control the thermal history of the specimens with greater precision. We also



anticipate that improving the purity of the additive formulation will partially alleviate the reduction in  $T_g$ , and so allow the reduction in CTE to be useful over a wider temperature range. Physical property analysis will also continue using the positron annihilation technique, and we will explore the applicability of the many other characterization techniques available in the Institute of Materials Science at the University of Connecticut. In particular, the promising results observed with the addition of fortifiers to rubber modified epoxies will necessitate an examination of the morphology of the cured polymer.

A longer term goal is to perform a chemical and structural analysis of the effect of a fortifier with a higher chemical functionality, since it is clear from earlier work that such materials provide a route for improved high temperature performance (5,6). Numerous options are indicated by the patents, but our primary criterion will be the ability to prepare the additive in a pure state, and to follow its reactions with available instrumentation.

The analysis of the mechanical performance of the bulk adhesive and the properties of adhesive joints clearly is far from complete. Some determination is required of the manner in which intentionally introduced flaws propagate in the adhesive. We intend to use a variant of the double cantilever beam experiment to obtain this information. In the longer term, it is also clear that wedge test data will be required to obtain information on the adhesive durability. Work with the present napkin ring joints will be continued, in particular with respect to the use of fortifiers as primers. It will be necessary to quantify and control the thickness of the primer layer to obtain a better quantitative description of this phenomenon. Parallel spectroscopic analysis using the internal reflection spectroscopy (IRS) technique will allow us to quantify the kinetics of interdiffusion of the primer and the adhesive (24). A more complete mechanical property analysis of the cured epoxy matrix is also required, particularly with respect to the response of the polymer to shear and compression forces, and the incorporation of these data into a more realistic model for the mechanical response characteristics of glassy polymers.

During the first six months of the project we have also made progress on the application of fortifiers to polyimides, although the results are outside the scope of this report. Durimid 100 (Rogers Corporation) and PI-2540 and 2545 (Dupont) show increases in modulus and suppression of low temperature relaxations, and interestingly little depression of  $T_g$ . We are exploring the effect of additive formulations based on a general sense on the epoxy experience. One property of particular interest is the CTE of the cured polyimide, and additives which reduce free volume and molecular mobility show promise in being able to produce a considerable improvement.

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